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13. ABSTRACT (Maximum 200 words) The polymerization of compounds containing the C=N bond is investigated. Two families of monomers are synthesized, namely imines (azaethylenes) and aza-1,3-dienes. For the imines, electron-accepting substituents such as cyano and carbomethoxy increase the polymerizability of these monomers. Extremely electrophilic imines are not stable, but do polymerize. Among the azadienes, the ones with the N-CN functionality are the most appropriate for polymerization. Substituents increase the stability of these dienes, but on the other hand hinder their polymerization and an exact balance has to be found.					
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Synthesis and Polymerization of Azaethylenes and Aza-1,3-dienes.

FINAL REPORT

H.K. Hall, Jr.

4/8/93

U.S. Army Research Office

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REPORT

STATEMENT OF PROBLEM

Even though much polymer chemistry involves polyaddition of C=C monomers and of C=O monomers, very little has been reported about monomers containing the C=N functionality. We have been carrying out an exploratory program on the synthesis and polymerization of suitably substituted imines and azadienes under USARO sponsorship. We have shown that proper choice of structure, initiator and conditions can give linear polymers. So far electron-accepting substituents, particularly cyano, and anionic initiators have given the best results. Moreover the publication of many recent organic chemistry papers describing the syntheses of such imines makes this a particularly opportune time to continue investigating their potential as new monomers. We applied insights from polymer chemistry to turn this growing body of knowledge to the synthesis of new, useful monomers and polymers.

ACCOMPLISHMENTS UNDER USARO SPONSORSHIP

Imine Monomers with one Electron-Accepting Group

The N-substituted imines $\text{CH}_2=\text{N-Acceptor}$, are far too reactive to permit isolation, purification and study of polymerization. Accordingly we placed substituents on the carbon to lower the reactivity into a reasonable range. As a first approach we only studied substituents without α -hydrogen to avoid a possible tautomerism to the enamide structure.



We synthesized a number of imines with two substituents: CN, COOMe or SO_2Me on N and Ph or tBu on C.

For the synthesis of these monomers we have recently developed a convenient straightforward procedure involving condensation of disilylcarbodiimide with the aldehyde in the presence of a catalytic amount of trimethylsilyl triflate. These imines were subjected to various initiators and best results were obtained in anionic homooligomerization. The best monomer among these imines was benzylidene cyanamide Ph-CH=N-CN . The polymers were white solids with softening points in the 170-250°C range.

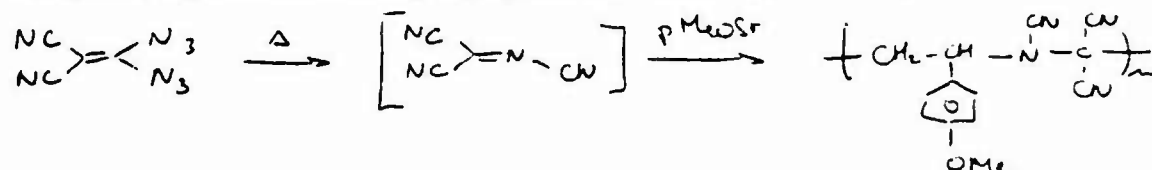
Thus the cyano group with its minimal steric requirements and strong ability to stabilize negative charge, emerged as the best of the electron-accepting groups to date. We have now prepared a variety of benzylidene cyanamide derivatives with substituents in the para position and these are currently under investigation.

Imine Monomers with Several Electron-Accepting Groups.

Extending our studies to imines containing electronegative substituents on both C and N, we first investigated tricarboethoxy methanimine. This imine proved to be too prone to

self-dimerization via the N-COOEt group to be used as a monomer.

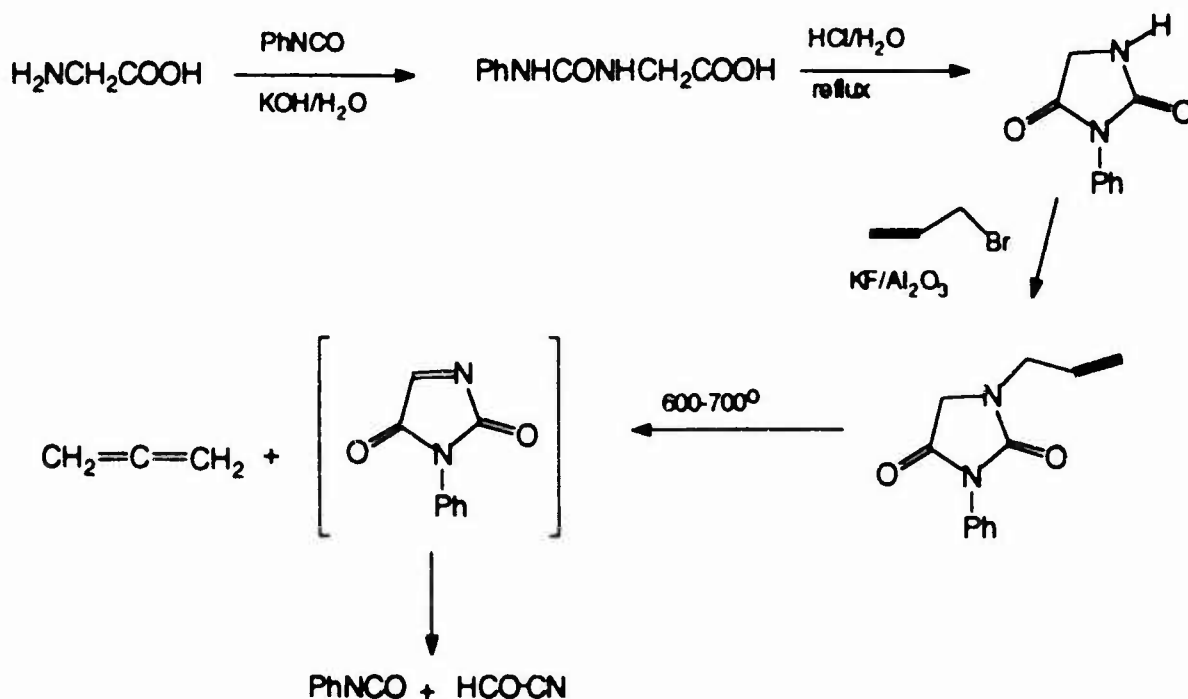
Because cyano groups are more electron-attracting than ester groups, we turned our attention to tricyanomethanimine C_4N_4 . After many attempts this monomer was finally synthesized by thermolysis of 1,1-diazo-2,2-dicyanoethylene. This highly electrophilic imine was stable in solution, but oligomerized upon attempted isolation. With p-methoxystyrene, high MW alternating copolymer was formed spontaneously.



Attempts to lower the reactivity of this trisubstituted imine by replacing cyano-groups by ester groups led us to synthesize $\text{MeOOC}(\text{NC})\text{C}=\text{N}-\text{CN}$, but this monomer is also too reactive to be isolated. The diester-monocyano derivative $(\text{MeOOC})_2\text{C}=\text{N}-\text{CN}$ was also too reactive.

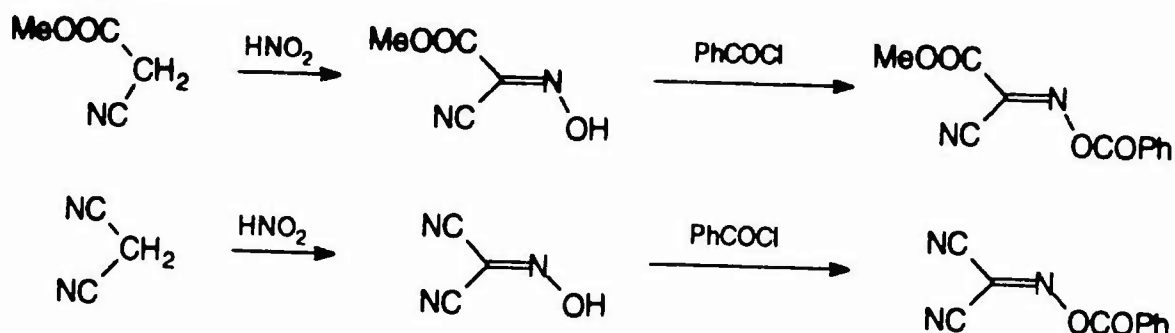
We also synthesized C,N-dicyano-methanimine, which is less electrophilic than C_4N_4 as shown by AM1 calculations. However the lower substitution pattern also results in lower stability, and the presence of this imine could only be confirmed by trapping with cyclopentadiene.

We did investigate the feasibility of synthesizing the cyclic imine N-phenyl dehydrohydantoin. Conventional synthesis methods involving oxidation of N-phenyl-2-azasuccinimide with DDQ or with sodium hypochlorite did not lead to any identifiable products. Therefore we did attempt to obtain this monomer by flash vacuum pyrolysis. The synthesis proceeds as follows: glycine was reacted with phenyl isocyanate in the presence of base, the resulting amide urea is treated with dilute acid at reflux and cyclization to N-phenylhydantoin occurs. This hydantoin is reacted with propargyl bromide in the presence of potassium fluoride on alumina to alkylate the N-position.



The flash vacuum pyrolysis was performed by Prof. Ripoll's laboratory at the University of Caen in France. They have the necessary equipment to trap the pyrolysis products at low temperature (180°K) and to take infrared, proton and carbon NMR at this low temperature. The allene and phenylisocyanate formed can be easily identified by their characteristic infrared spectra. A peak at 8.95 ppm in the proton NMR could be ascribed to the desired compound, but this peak disappeared above 180°K. This would indicate that the desired N-phenyl dehydrohydantoin is much too reactive to exist at room temperature and thus it is not possible to use it as a novel monomer.

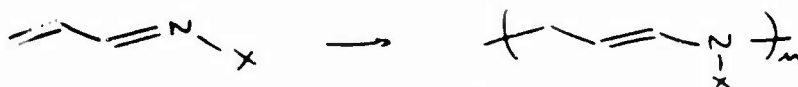
Another series of imines we investigated are derivatized from N-hydroxyimines. Malononitrile or methyl cyanoacetate are reacted with nitrous acid to form the corresponding oxime. The hydroxyl group can then be esterified with either benzoyl chloride or p-nitrobenzoyl chloride.



Upon trying to polymerize these novel imines, only very low yields of oligomers were obtained in all areas.

1-Aza-1,3-butadiene Monomers with Electron-Accepting Group on N

Azabutadienes were investigated because a vinyl group might act as a "handle" for polymerization of the C=N bond. If such monomers polymerize by 4,1-addition, this will be evidence for polymerization of C=N by the particular mechanism employed.



The original synthesis route we used to obtain these monomers involved pyrolysis of the cyclopentadiene adducts. Thus, N-carboethoxy-3-methyl-1-aza-1,3-butadiene was synthesized starting from 5-methyl-2-norbornene-5-carboxaldehyde and ethyl carbamate. N-Carboethoxy-3-methyl-1-azabutadiene undergoes anionic polymerization to form polymers with MW up to 2,000 with softening points around 150°C. Free radical polymerization was less satisfactory. The structure of the polymer resulted from both 4,1- and 4,3-addition.

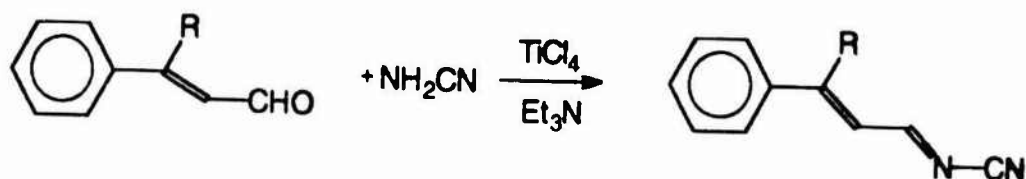


More recently we have developed a more straightforward and versatile synthesis into this class of monomers by direct condensation of aldehydes with appropriate amine

derivatives in the presence of catalytic or equivalent amount of Lewis acid. In this way we have recently synthesized, among others, crystalline N-phenylsulfonyl-3-methyl-1-azabutadiene. This new approach will be further discussed in the proposed research.

N-Phenylsulfonyl-3-methyl-1-azabutadiene oligomerized in the presence of anionic initiators. No radical polymerization was observed. However in free radical copolymerization with styrene and p-methoxystyrene, nearly alternating copolymers of high MW were formed.

Cyano-4-phenyl-1-azabutadiene and N-cyano-3-methyl-4-phenyl-1-azabutadiene were both obtained from reaction of cyanamide in the presence of titanium tetrachloride and triethylamine (DABCO) with cinnamaldehyde and β -methyl-cinnamaldehyde respectively. Both these azadienes could be purified.



R = H, Me

Neither azadiene would homopolymerize under either free radical or anionic conditions. With allylmagnesium bromide a small amount of oligomer of the methyl-substituted azadiene was obtained. No cycloaddition products were obtained with either cyclopentadiene or furan. However with p-methoxystyrene, styrene or ethyl vinyl ether, after 20 hours at 80°C in benzene, the [4+2] Diels-Alder cycloadduct was obtained in all cases. Some of these adducts were crystalline solids. All adducts were fully characterized by NMR spectroscopy. The reactivity of these electrophilic azadienes in Diels-Alder reactions are in agreement with the behavior of other electrophilic azadienes described in the literature. The lack of polymerizability can be attributed to the number of substituents. A compromise will have to be found: more substituents stabilize the azadiene structure, but they hinder their polymerizability.

1-Azabutadiene Monomers with Aryl Groups on N

Again our original syntheses involved pyrolyses of cyclopentadiene adducts, which were obtained from reaction of cyclopentadiene with acrolein and subsequent reaction with the appropriate amine. In this case too our new direct condensation of (meth)acrolein with aniline in the presence of the Lewis acid TiCl_4 leads to higher yields and easier access to different structures.

Anionic polymerization of N-phenyl- and N-(2,4,6-trimethylphenyl)-1-aza-1,3-butadiene succeeded, leading to polymers with molecular weights up to 5,000. Clean 4,1-propagation was observed with the N-phenyl monomer at 0°C using n-BuLi as initiator. Free radical polymerization does not occur, probably due to excessive stabilization of the azaaryl radical, as also observed in the all-carbon analog 1-phenylbutadiene.⁴

2-Azabutadiene Monomers with Aryl Groups on N

Using the pyrolysis route, we synthesized 1-phenyl-2-aza-1,3-butadiene⁴ and briefly studied its polymerization behavior. Low molecular weight polymers are obtained in high yield with anionic initiators at low temperature.

o-Phthalaldehyde Diimines

The known high polymerizability of o-phthalaldehyde is ascribed to the close proximity of the two aldehyde functions and to the fact that cyclopolymerization occurs. In analogy to this, we tried to synthesize several diimine derivatives of o-phthalaldehyde⁵. However all attempts to obtain these o-diimines failed and only led to addition products, Cannizzaro-like redox reactions, etc.

Publications under USARO Sponsorship

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6. B. Roekens, A.B. Padias and H.K. Hall, Jr. "C,N-Dicyanomethanimine", J. Chem. Res. (1993, in press).

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